Gaseous ion film-plating method and device thereof

(pertinent parts referred to by the Examiner, pages 3-5 and claim 2)

As for the gaseous substances and vaporized substances to the added, they are selected mainly based on physical and chemical properties of the desired film. For example,

1. To input only nitrogen and hydrogen gas to nitridize a pre-set metal workpiece (expressed as A), thereby forming a metallic or nonmetallic nitride film on the workpiece, the reaction being as follows:

$2A + N_2 + H_2 \longrightarrow 2AN + H_2$

2. To simultaneously input vaporized halide and gaseous substances such as nitrogen, hydrogen or acetylene, methane, to produce in plasma state metal nitride, carbide or boride, which deposit on surface of the workpiece and form different plated films, for example

$BCl_3 + H_2 + N_2 + Ar \longrightarrow BN + HCl + Ar$

$TaCl_5 + CN_4 + Ar \longrightarrow TaC + HCl + Ar$

$CrCl_3 + TiCl_4 + H_2 + N_2 + Ar \longrightarrow (Cr_xTi_y)N_{(1-x+y)} + HCl + Ar$

wherein, $x \geq 0$, $y \geq 0$, and $x+y < 1$.

The present method is performed by using the following device:

As shown in Fig. 1, the device consists of a gas source cabinet (1), a gas flow controller (2), a liquid storing and atomizing means (3), a vacuum chamber (5), a vacuum pump (7) and an electric control box (8). The gas source cabinet (1) is connected to the vacuum pump (5) via the gas flow controller (2), and argon source in the gas source cabinet (1) is connected to the liquid storing and atomizing means (3) via the gas flow controller (2) and then connected to the vacuum chamber (5). The vacuum chamber (5), inside, is equipped with a workpiece frame (9), an electric heating element (10) and an electrode net (11) that are alternately arranged in layers. The workpiece frame (9) and the electrode

net (11) are connected to a high-voltage direct current generator of the electric control box (8). On the top of the vacuum chamber (5) a thermal controller (12), a vacuum gauge (13) and a release valve (14) are installed.

The device operates in such a way: to place a workpiece to be plated or a workpiece on which a substrate has been plated on the workpiece frame (9) in the vacuum chamber (5), close the vacuum chamber (5), start the vacuum pump (7) to make the vacuum chamber (5) reach a vacuum of 10^{-1}-10^{-2} Pa, and simultaneously turn on the electric heating element (10) to heat the workpiece to a predetermined temperature and keep it at the temperature for a certain period of time. Then, to input gaseous substances as reactants to the vacuum chamber (5), adjust their flow and keep the vacuum chamber (5) at the required vacuum, if necessary, input halide(s), and place liquid substances such as halide(s) in the liquid storing and atomizing means (3), and charge argon and atomize it before inputting it to the vacuum chamber (5). Subsequently, to impose direct current voltage between the wokpiece frame (9) and the electrode net (11) in the vacuum chamber (5), to ionize the gas into plasma, and keep the plasma stable until the plated film reaches the requirement, turn off power, and remove the workpiece.

Fig. 1 shows the working principle of the device used in the present invention.
Fig. 2 shows the planform of the internal structure of the vaccum chamber (5).
Fig. 3 shows the cutaway view of the liquid storing and atomizing means.

In use, the workpiece frame (9), the electric heating element (10) and the electrode net (11) in the vacuum chamber (5) may be installed transversely or vertically, preferably vertically, and the workpiece frame (9) may be designed to be movable, for the convenience of placing workpiece. Preferably, the electric heating element (10) uses a far-infrared heating pipe, to increase thermal

efficiency. To save space, the electric heating element (10) may be supported on the electrode net (11), to shorten the distance among the workpiece frame (9), the electric heating element (10) and the electrode net (11), thereby increasing thermal efficiency and film-plating speed. In order to increase the deposition speed of plasma, the workpiece (9) is preferably connected to negative high voltage of the high-voltage direct current generator. In order to reduce pollution of residual gas to environment, a waste gas purifier (6) is preferably installed in series to the pipeline between the vacuum chamber (5) and the vacuum pump (7). A gas release valve (14) is further installed on top of the vacuum chamber (5) in order to release air into the vacuum chamber (5) when it is open. The liquid storing and atomizing means (3) may be a common atomizer or has a structure shown in Fig. 3. The means consists of a tank (3a), a gas inlet pipe (3b) inserting in the tank (3a) to its lower part, and a gas outlet (3c) at upper part of the tank (3a). The tank (3a) contains liquid (3d) as reactant. In use, argon enters the tank (3a) via the gas inlet pipe (3b), passes through the liquid (3d) layer and carries the liquid (3d) as reactant to enter the vacuum chamber (5) via the gas outlet (3c). A water tank (3f), which includes inside an electric heating element (3e) and a temperature controller, is preferably further installed outside of the liquid storing and atomizing means (3), so that low-melting point reactants that are solid at normal temperature and normal pressure is heated to liquid. In order to mix various gaseous substances that take part in the reaction, a gas mixer (4) is preferably further installed in front of a gas inlet (5a) of the vacuum chamber (5). The gas mixer (4), which is a vessel with a cavity having a relatively larger volume, includes a gas inlet and a gas outlet, wherein the gas inlet is connected to various gas input pipes, and the gas outlet is connected to the vacuum chamber (5). An insulating layer (15) is further installed on the casing of the vacuum chamber (5), to prevent emission of heat and increase thermal efficiency.

As compared with the prior art, the present invention has the following advantages:

1. Due to elimination of electronic gun, removal of solid target electrode and target power source, without rotation and revolution of the workpiece, the device is characterized in simple structure, convenient operation and low cost.

2. Due to the use of gaseous raw materials, the reactants have good dispersibility, are independent of shape and size of the workpiece, can form film with uniform thickness and color, and can plat film on workpiece having larger size and complicated shape.

3. Due to the use of ionization-discharge and electric field adsorption process for plating film, the plated film is characterized in a stronger binding force with the substrate, better chemical stability and not easy to change and lose color, as compared with that obtained by using the existing film plating process.

4. The gaseous raw materials are easily changed, and can plat, on requirement, various films having different physical/chemical properties and different colors at any moment, so their application range is very broad.

The following example serves to further illustrate the invention (the volume of vacuum chamber is 1.1 m^3).

1. TiN is plated on surface of an iron-based workpiece by the steps of:

a. to place a workpiece on a workpiece frame (9), and put it in a vacuum chamber (5);

b. to start a vacuum pump (7) to make the vacuum chamber (5) reach a vacuum of 10^{-1} Pa;

c. to turn on an electric heating element (10) to make the temperature on surface of the workpiece reach about 500°C;

d. to input $TiCl_4$ in a liquid storing and atomizing means (3);

e. to turn on a gas flow controller (2) to adjust flow of various gases.......

Claims

2. A gaseous ion film-plating device, which consists of a gas source cabinet (1), a gas flow controller (2), a liquid storing and atomizing means (3), a vacuum chamber (5), a vacuum pump (7) and an electric control box (8); wherein the gas source cabinet (1) is connected to the vacuum pump (5) via the gas flow controller (2), and argon source in the gas source cabinet (1) is connected to the liquid storing and atomizing means (3) via the gas flow controller (2) and then connected to the vacuum chamber (5); the vacuum chamber (5) is equipped with, inside, a workpiece frame (9), an electric heating element (10) and an electrode net (11) that are alternately arranged in layers; the workpiece frame (9) and the electrode net (11) are connected to a high-voltage direct current generator of the electric control box (8); on top of the vacuum chamber (5) a thermal controller (12), a vacuum gauge (13) and a gas release valve (14) are installed.

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[71]申请人 冯安文
地址 510180广东省广州市人民中路白沙巷23号二楼

[72]发明人 冯安文 沈名强 刘志心

[74]专利代理机构 广东专利事务所
代理人 何本谋

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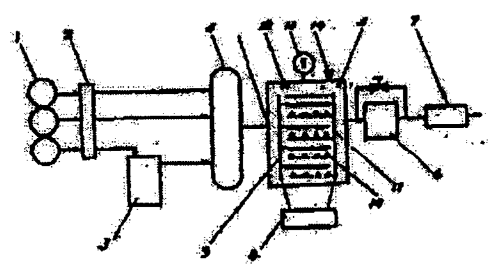
[54]发明名称 气相离子镀膜方法与其装置

[57]摘要

本发明提供一种气相离子镀膜方法及其装置。该方法是在低真空度和一定温度的状态下，通过高压电场作用，将气态物质电离，形成等离子体，并在电场作用下使单质等离子体，经反应的化合物镀于工件表面。该方法所使用的设备主要有气源柜、气体流量控制器、溶液及液体雾化装置、真空室、真空泵和电控柜组成。在真空室内设有工件架、电热元件和电极网。该发明具有工艺与设备简单、操作方便、成本低、镀膜均匀和牢固以及应用范围广等优点。



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气相离子镀膜方法及其装置

本发明属于一种改进的镀膜方法及装置，特别是一种气相镀膜方法及其设备，适合于金属产品、镀膜。

在现有技术中，金属表面镀膜的方法主要有三种：其一是液体电镀，缺点是严重污染环境，易氧化变色、不耐用；其二是溅射镀、多弧度氮化钛和碳化钛，该方法是利用电子或离子轰击置于真空室内的钛靶，使钛溅射到工件表面形成膜层，但不足的是工件要作自转和公转运动，工艺复杂、效率低、成本高、膜层不均匀，难以在体积较大、形状复杂的工件上镀膜，而且镀层颜色单一、色泽亦不够鲜明；其三是化学气相镀膜法，其原理是利用气态物质在固体表面进行化学反应，生成固态化合物膜层的方法，该方法的缺陷是需要较高的反应温度，很容易使工件产生变形，而且加热装置复杂、耗能大，难以在生产中推广应用。

本发明的目的在于克服已有各种金属镀膜方法之不足，提供一种工艺较为简单、操作方便、对工件形状适应性好、镀层牢固、颜色多样而鲜明的气相离子镀膜方法及其装置。

本发明的任务是这样实现的：

将待镀的工件悬置于真空室内，将工件加热至200—600°C，并恒定在指定的温度，往真空室内输入所需要的气体、汽化物质，并使真空室内保持100Pa—1Pa的真空度，与此同时，在真空室内的电极与工件之间输入300—1200V的直流高压，使气体、汽化物质电离成等离子体，在电场力的作用下使单质的等离子体、经化学反应后形成的化合物、络合物沉积于工件表面而形成各种所需要的镀膜层。

来选择。例如

1、只输入氮、氢气体，使之与预置的金属工件（以A表示）起氮化反应，在工件上便可形成金属或非金属的氮化膜层，其反应如下：

$$2A+N_2+H_2 \longrightarrow 2AN+H_2$$

2、同时输入汽化的卤化物以及氮、氢或乙炔、甲烷等一些碳氢化合物气体，在等离子态下生成金属氮化物、碳化物或硼化物，沉积于工件表面形成不同的镀膜层。例如

$$BCl_3+H_2+N_2+Ar \longrightarrow BN+HCl+Ar$$

$$TaCl_5+CH_4+Ar \longrightarrow TaC+HCl+Ar$$

$$CrCl_3+TiCl_4+H_2+N_2+Ar \longrightarrow (Cr_xTi_y)N(1-x+y)+HCl+Ar$$

其中：$x>0$，$y>0$而且$x+y<1$

本工艺方法是采用如下装置来进行的：

如图1所示，该装置由气体柜（1）、气体流量控制器（2）、储液及液体雾化装置（3）、真空室（5）、真空泵（7）和电控柜（8）组成，气源柜（1）通过气体流量控制器（2）与真空泵（5）连接，其中气源柜（1）中的氢气源通过气体流量控制器（2）与液及液体雾化装置（3）连接再与真空室（5）连接，在真空室（5）内装有分层交替相间设置的工件架（9）、电热元件（10）和电极网（11），工件架（9）和电极网（11）与电控柜（8）的高压直流发生器连接，在真空室（5）上部装有温控器（12）、真空表（13）及放气阀（14）。

本装置是这样工作的：将待镀的工件或已镀衬底的工件置于真空室（5）内的工件架（9）上，关闭真空室（5），启动真空泵（7）使真空室（5）的真空度达10^{-1}—$10^{-2}Pa$，同时接通电热元件（10）加热工件到予置的温度并保温一段时间，然后往真空室（5）输入参与反应的气态物质，并

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便使一些常温常压下为固体的低落点反应物质加热成液体。为了便于各种参与反应的气相物质的混合，在真空室(5)的进气口(5a)的前端最好增设一个气体混合器(4)，该气体混合器(4)为一个体积比较大的空腔容器，设有进气口和出气口，进气口与各反应气体输入管连接，出气口与真空室(5)连接。在真空室(5)的外壳上还设有一隔热保温层(15)，以防止热量散失，提高热效率。

本发明与现有技术相比，具有如下优点：

1、由于本发明淘汰了电子枪，取消固体的靶电极、靶电源，工件不需要自转和公转，因而所用装置结构简单、操作方便、成本低。

2、由于采用气相原料，反应物的弥散性好，不受工件的形状和尺寸影响，镀膜层的厚度和色泽均匀，可对尺寸较大和形状复杂的工件进行镀膜。

3、由于本发明是采用电离放电和电场吸附的方法进行镀膜，其镀膜与基体的结合力比现有镀膜方法牢固，化学稳定性好，不易变色和退色。

4、本发明的气相原料很容易更换，可随时根据需要镀出各种不同物理化学性能和不同颜色的膜层，因此其应用范围十分广泛。

以下举出几个实施例（真空室的容积为1.1米^3）：

1、在铁基工件表面镀TiN，其工艺过程是：

a、将工件置于工件架(9)上，移进真空室(5)内。

b、启动真空泵(7)，使真空室(5)的真空度达10^{-3}Pa。

c、接通电热元件(10)，使工件表面温度达500°C左右。

d、在储液及液体雾化装置(3)中加入$TiCl_4$。

e、开启气体流量控制器(2)，调节各气体的流量：N_2(3.5升/小时)，

c、加热工件至[illegible]°C。

d、输入[illegible]$_2$(1升/小时)、[illegible]$_2$(6升/小时)、Ar(1升/小时)，并维持室内真空度[illegible]Pa。

e、接通高压电源输入[illegible]V的直流高压，维持30分钟。

f、关机取出工件。

本发明及其装置适合于在金属产品上镀各种装饰性的防锈膜、仿金膜等。

说 明 书 附 图

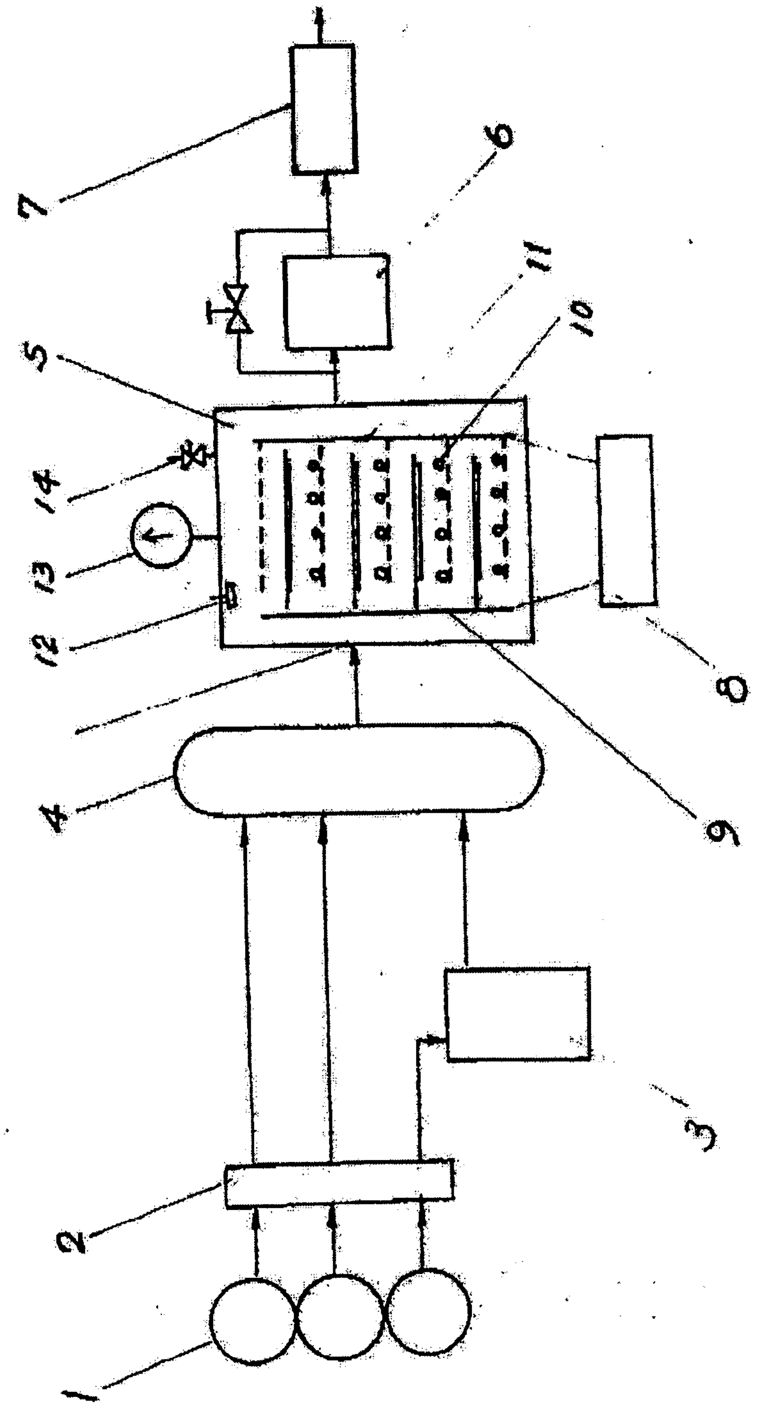

图 1